

2

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 17710.2-CH	2. GOVT ACCESSION NO. ADN/A 119040	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) Photodecomposition of Methyl Nitrite Trapped in Solid Argon		5. TYPE OF REPORT & PERIOD COVERED Reprint
		6. PERFORMING ORG. REPORT NUMBER N/A
7. AUTHOR(s) Marilyn E. Jacox Frederick L. Rook		8. CONTRACT OR GRANT NUMBER(s) ARO 27-82
		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS N/A
9. PERFORMING ORGANIZATION NAME AND ADDRESS National Bureau of Standards Washington, DC 20234		12. REPORT DATE 1982
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709		13. NUMBER OF PAGES 6
		15. SECURITY CLASS. (of this report) Unclassified
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Submitted for announcement only.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DTIC ELECTE SEP 8 1982 S D B		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		

AD A119040

DTIC FILE COPY

Published in Journal of Physical Chemistry, July 22, 1982, 2899-2904, by the American Chemical Society

Photodecomposition of Methyl Nitrite Trapped in Solid Argon

Marilyn E. Jacox* and Frederick L. Rook†

Molecular Spectroscopy Division, National Bureau of Standards, Washington, D.C. 20234 (Received: December 11, 1981;
In Final Form: February 1, 1982)

The threshold wavelength for the photolysis of methyl nitrite isolated in solid argon at 14 K has been determined to be near 370 nm. Photolyzed samples show prominent infrared absorptions of H_2CO and HNO , which are perturbed by the hydrogen-bonding interaction of these two molecules trapped in adjacent sites. In studies with 122- and 105-nm radiation sources and with concurrent deposition and photolysis, some of the H_2CO escapes interaction with HNO . Similar observations result on photolysis of methyl- d_3 nitrite. Time dependence studies show that in the early stages of photolysis the *trans*- CH_3ONO absorptions grow at the expense of those of the *cis* rotamer. The stabilization of H_2CO and HNO is consistent with gas-phase observations, which have demonstrated that the primary products of the photodecomposition of both *cis*- and *trans*- CH_3ONO are $\text{CH}_3\text{O} + \text{NO}$, which can recombine with zero activation energy either to re-form CH_3ONO or to form $\text{H}_2\text{CO} + \text{HNO}$. The cage recombination of CH_3O and NO to form these same products should predominate in the decomposition of methyl nitrates in other condensed-phase systems. The possible deactivation of electronically excited methyl nitrite into lower electronic states or into excited vibrational levels of the ground electronic state which favor direct decomposition into $\text{H}_2\text{CO} + \text{HNO}$ is considered.

Introduction

Because methyl nitrite is a potential source of the methoxy (CH_3O) free radical, important in such diverse chemical processes as atmospheric pollution, combustion, and propellant ignition, its photochemistry has been the subject of several studies. Classical end-product analysis studies, summarized by Calvert and Pitts,¹ have determined that the predominant primary process results in the formation of $\text{CH}_3\text{O} + \text{NO}$. Hecklen and co-workers^{2,3} have found a quantum yield of 0.76 for this process at 25 K using 366-nm radiation. A new generation of studies, with the advantage of direct detection of transient molecules, began with the flash photolysis experiments of Napier and Norrish,^{4,5} who detected H_2CO and NO and assigned a

207–291-nm band system to nitrosoformaldehyde. Subsequent studies by Callear and Wood⁶ demonstrated that these bands were contributed by HNO . In a study of the emission spectrum resulting on photolysis of methyl nitrite, Tanaka and co-workers⁷ observed a threshold of 6.02 eV (206 nm) for the appearance of emission bands previously

(1) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry", Wiley, New York, 1966, pp 480–3.

(2) H. A. Wiebe and J. Hecklen, *J. Am. Chem. Soc.*, **95**, 1 (1973).

(3) H. A. Wiebe, A. Villa, T. M. Hellman, and J. Hecklen, *J. Am. Chem. Soc.*, **95**, 7 (1973).

(4) I. M. Napier and R. G. W. Norrish, *Proc. R. Soc. (London)*, **Ser. A**, **299**, 317 (1967).

(5) I. M. Napier and R. G. W. Norrish, *Proc. R. Soc. (London)*, **Ser. A**, **299**, 337 (1967).

(6) A. B. Callear and P. M. Wood, *Trans. Faraday Soc.*, **67**, 3399 (1971).

(7) K. Ohbayashi, H. Akimoto, and I. Tanaka, *J. Phys. Chem.*, **81**, 798 (1977).

* Present address: Department of Electrical Engineering, University of Virginia, Charlottesville, VA 22901.

attributed to CH_3O .⁸ Subsequently, both the assignment of these bands to CH_3O ^{9,10} and the threshold for the formation of electronically excited CH_3O ¹¹ were confirmed. Recently, Sanders and co-workers¹² have used laser-excited fluorescence to monitor both the CH_3O produced by the 266-nm photolysis of methyl nitrite and the HNO produced in the important secondary reaction of CH_3O with NO to produce H_2CO and HNO .

The immobilization of methyl nitrite molecules in an argon matrix would greatly reduce the possibility for secondary reactions which typically lead to the formation of such products as methanol and nitrous oxide. However, because the CH_3O and NO radical fragments are trapped in adjacent sites, efficient recombination would occur. In the argon-matrix study by Brown and Pimentel,¹³ peaks assigned by Tarte¹⁴ to *cis*- CH_3ONO , presumed to be the more stable rotamer, disappeared much more rapidly than did those of *trans*- CH_3ONO . Although this assignment has since been questioned,^{1,4} recent microwave studies^{15,16} have verified it. The appearance of prominent absorptions of H_2CO and of HNO when methyl nitrite was photolyzed and the relatively rapid disappearance of *cis*- CH_3ONO led Brown and Pimentel to suggest a photolysis mechanism in which the *cis* rotamer could either rearrange to the *trans* structure or photodecompose into $\text{H}_2\text{CO} + \text{HNO}$, whereas the *trans* rotamer photodecomposed to produce $\text{CH}_3\text{O} + \text{NO}$.

Important information regarding the products and mechanism of photodecomposition of methyl nitrite may result from more detailed studies of its photolysis in an argon matrix. The cage recombination of $\text{CH}_3\text{O} + \text{NO}$ is common to the argon matrix and to other condensed-phase systems, including the first stages of propellant ignition and explosive detonation. With suitable sampling and photolysis conditions, infrared spectral data may possibly be obtained for the important reaction intermediate CH_3O and for identification of the carrier of two absorptions which no longer can be attributed to HNO .^{17,18} The results of such a more detailed study are presented in the following discussion.

Experimental Details²³

Samples of CH_3ONO and CD_3ONO were synthesized and purified with procedures similar to those described by Sanders.¹² In the synthesis of CD_3ONO , D_2O was used as the solvent and all reagents except the nitrosyl sulfuric acid were fully deuterated. The infrared spectra of the resulting samples, considered in detail in a separate publication,¹⁹ showed no extraneous absorptions. Gas samples with an $\text{Ar}:\text{CH}_3\text{ONO}$ or $\text{Ar}:\text{CD}_3\text{ONO}$ mole ratio of 200 were prepared by direct sampling of methyl nitrite at a pressure of approximately 4 torr and addition of approximately 800 torr of argon.

- (8) D. W. G. Style and J. C. Ward, *Trans. Faraday Soc.*, **49**, 999 (1953).
- (9) G. Inoue, H. Akimoto, and M. Okuda, *Chem. Phys. Lett.*, **63**, 213 (1978).
- (10) G. Inoue, H. Akimoto, and M. Okuda, *J. Chem. Phys.*, **72**, 1769 (1980).
- (11) F. Lahmani, C. Lardeux, M. Lavollee, and D. Solgadi, *J. Chem. Phys.*, **73**, 1187 (1980).
- (12) N. Sanders, J. E. Butler, L. R. Pasternack, and J. R. McDonald, *Chem. Phys.*, **48**, 203 (1980).
- (13) H. W. Brown and G. C. Pimentel, *J. Chem. Phys.*, **29**, 883 (1958).
- (14) P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1952).
- (15) W. D. Gwinn, R. J. Anderson, and D. Stelman, *Bull. Am. Phys. Soc., Ser. II*, **11**, 831 (1966).
- (16) P. H. Turner, M. J. Corkill, and A. P. Cox, *J. Phys. Chem.*, **83**, 1473 (1979).
- (17) M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.*, **48**, 536 (1973).
- (18) P. N. Clough, B. A. Thrush, D. A. Ramsay, and J. G. Stamper, *Chem. Phys. Lett.*, **23**, 155 (1973).
- (19) F. L. Rook and M. E. Jacox, *J. Mol. Spectrosc.*, **93**, 101 (1982).

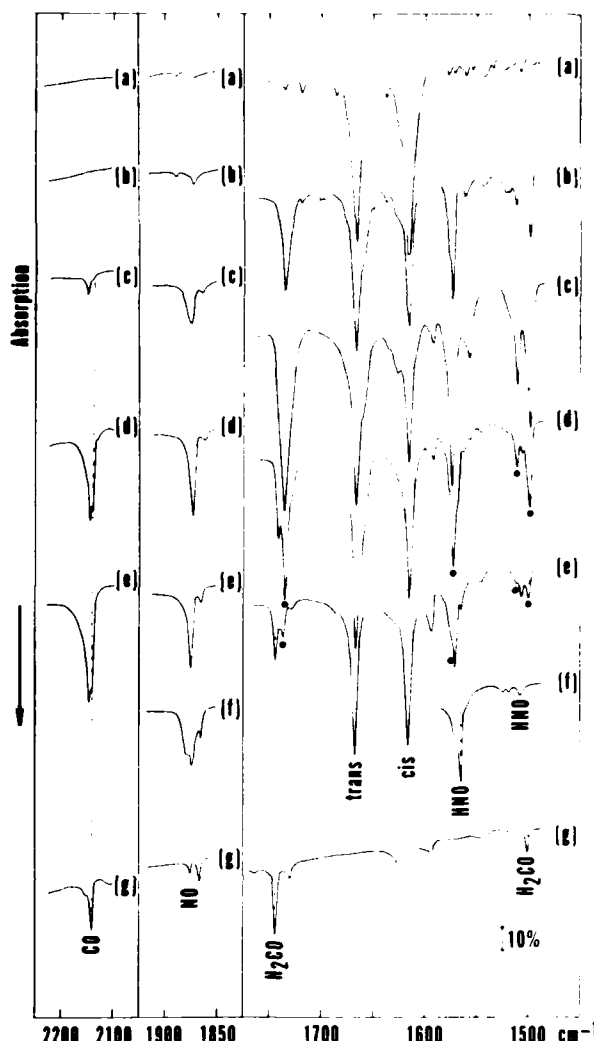


Figure 1. (a) 3.00 mmol $\text{Ar}:\text{CH}_3\text{ONO} = 200$ deposited at 14 K without photolysis. (b) 64-min subsequent mercury-arc photolysis ($\lambda > 300$ nm) of sample in (a). (c) 3.53 mmol $\text{Ar}:\text{CH}_3\text{ONO} = 200$ deposited at 14 K over period of 237 min with concurrent unfiltered mercury-arc photolysis. (d) 2.89 mmol $\text{Ar}:\text{CH}_3\text{ONO} = 200$ deposited at 14 K over period of 174 min with concurrent hydrogen-discharge photolysis. (e) 2.89 mmol $\text{Ar}:\text{CH}_3\text{ONO} = 200$ codeposited at 14 K over period of 199 min with 2.35 mmol discharged Ar . (f) 13.3 mmol $\text{Ar}:\text{NO} = 400$ codeposited at 14 K over period of 376 min with 11.7 mmol discharged $\text{Ar}:\text{H}_2 = 200$. (g) 4.81 mmol $\text{Ar}:\text{CH}_3\text{OH} = 200$ codeposited at 14 K over period of 245 min with 1.82 mmol discharged Ar . (●) Grows on subsequent mercury-arc photolysis.

The cryogenic equipment and sample observation configuration used for these experiments have previously been described.²⁰ All observations were conducted at 14 K. Photolysis sources included a medium-pressure mercury arc, a microwave-powered hydrogen discharge,²¹ and a beam of argon atoms excited by a microwave discharge and codeposited with the sample.^{20,22} In many of the mercury-arc photolysis experiments, a Corning 7380 glass filter was used to exclude radiation of wavelength shorter than 345 nm from the sample. Corning 3060 and 0160 glass filters, with short-wavelength cutoffs of 370 and 300 nm, respectively, were also used. In some of the experiments the entire sample was deposited before photolysis, while

(20) M. E. Jacox, *Chem. Phys.*, **7**, 424 (1975).

(21) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 5146 (1967).

(22) M. E. Jacox, *Rev. Chem. Intermed.*, **2**, 1 (1978).

TABLE I: Peak Optical Densities of CH₃ONO Photolysis Products Trapped in Solid Argon

cm ⁻¹	$\lambda > 300^a$	$\lambda > 250^b$	$\lambda > 122^b$	$\lambda > 105^b$	assignment
1499	0.162	0.371	0.235	0.050	H ₂ CO
1512	0.052	0.225	0.078	0.011	HNO ^c
1571				0.229	HNO ^d
1574	0.420	0.699	0.400	sh	HNO ^c
1736	0.335	1.036	0.541	0.049	H ₂ CO ^c
1744			sh	0.155	H ₂ CO
1875	0.028	0.089	0.218	0.255	NO
2148		0.055	0.200	0.258	CO

^a Photolysis of total sample. ^b Photolysis concurrent with deposition. ^c Site I; HNO + H₂CO pair interactions. ^d Site II.

in others photolysis was conducted concurrently with deposition.

Infrared spectra of the solid deposits were recorded with a Beckman IR-9 infrared spectrophotometer. Under the scanning conditions used for these experiments, the resolution and relative and absolute frequency accuracies are estimated to be 1 cm⁻¹ between 400 and 2000 cm⁻¹ and 2 cm⁻¹ between 2000 and 4000 cm⁻¹.

Observations

Regions of especial interest in the spectrum of a simple Ar:CH₃ONO = 200 deposit at 14 K are shown in trace a of Figure 1. The only prominent absorptions in the spectral regions here considered are the very intense N=O stretching absorption of *cis*-CH₃ONO, at 1620 cm⁻¹, and its somewhat less intense counterpart for the *trans* rotamer, at 1677 cm⁻¹. The weak pattern of peaks between 1500 and 1600 cm⁻¹ is contributed by incompletely compensated water vapor in the spectrophotometer.

When such a deposit was subjected to filtered mercury-arc radiation of wavelength longer than 370 nm, the infrared spectrum was unchanged. However, when a filter with a short wavelength cutoff of 345 nm was used, permitting access of the 366-nm mercury-arc radiation to the sample, photolysis occurred, indicating that predissociation occurs in the long wavelength methyl nitrite band system reported by Calvert and Pitts.²³ The photolytic behavior of deposits exposed to radiation of wavelength longer than 300 nm, such as the sample of trace b, was identical with that observed when the 345-nm cutoff filter was used. Upon photolysis, there was a marked decrease in the intensities of the absorptions of *cis*-CH₃ONO, exemplified by the 1620-cm⁻¹ absorption of trace b, but the intensities of the absorptions of the *trans* rotamer changed relatively slowly. The positions and peak optical densities of the product absorptions shown in trace b are summarized in the first two columns of Table I. In addition, very strong absorptions appeared at 2812 and 2880 cm⁻¹, moderately intense absorptions at 1174 and 1248 cm⁻¹, a weak to moderately intense peak at 1029 cm⁻¹, and weak peaks at 1109, 2724, and 3450 cm⁻¹. Absorptions at 1125, 1353, 1550, 2151, 2267, 3005, and 3300 cm⁻¹, for which Brown and Pimentel¹³ reported peak optical densities equal to or greater than 0.03 in photolyzed Ar:CH₃ONO samples, did not appear.

The relatively weak product absorption at 1875 cm⁻¹ is readily assigned to NO. As in the studies of Brown and Pimentel, absorptions of HNO and of H₂CO were expected to be prominent. Trace f shows the absorption spectrum which resulted in a study¹⁷ of the reaction of H atoms, produced in a microwave discharge, with NO isolated in

an argon matrix. The peaks assigned to isolated HNO, at 1505 and 1563.5 cm⁻¹, are significantly shifted from the prominent absorption maxima at 1512 and 1574 cm⁻¹ in the methyl nitrite experiments. The 2716-cm⁻¹ absorption of HNO isolated in solid argon¹⁷ is shifted to 2724 cm⁻¹ in the present experiments and is considerably weaker than would be expected for the unperturbed molecule. The absorptions at 1174, 1248, 1499, 1736, 2812, and 2880 cm⁻¹ correspond reasonably well with the fundamentals of gas-phase H₂CO.²⁴ Trace g of Figure 1 shows two of the fundamental absorptions of H₂CO isolated in solid argon following the interaction of CH₃OH with a beam of excited argon atoms.²⁵ While an absorption appears at 1499 cm⁻¹ in both trace b and trace g, the shift of the very prominent 1736-cm⁻¹ absorption of trace b from the 1744-cm⁻¹ absorption of H₂CO isolated in solid argon is several times as great as the combined uncertainties for the two spectral scans. Of the remaining product absorptions, the most prominent is the peak at 1029 cm⁻¹.

The proximity of the most prominent product absorptions to those previously reported for H₂CO and HNO and the importance of these two molecules in previous studies of the photodecomposition of methyl nitrite dictate the assignment of the observed absorptions to these two products. In the matrix study on HNO,¹⁷ the positions and relative intensities of its absorptions were extremely sensitive to the presence of traces of nitrogen in the sample. The positions of the fundamental absorptions of a molecule of H₂CO isolated in an argon matrix are also significantly shifted on interaction with another H₂CO molecule trapped in an adjacent site.²⁶ It is suggested that the shift in the absorptions of HNO and H₂CO in the present study results from the hydrogen bonding of these two molecules trapped in adjacent sites in the argon matrix.

In the experiment of trace c, the sample was irradiated by the full light of the medium-pressure mercury arc during deposition. As is shown in the third column of Table I, the product yield was substantially higher than in the filtered photolysis study, but the only new product absorptions were a rather broad, moderately intense peak at 1558 cm⁻¹ and the 2148-cm⁻¹ peak of CO.

Portions of the spectrum of a sample deposited with concurrent photolysis by 122-nm hydrogen-discharge radiation are shown in trace d, and the corresponding peak optical densities are summarized in the fourth column of Table I. The intensities of the absorptions of CO and of NO are several times as great in this experiment as in that of trace c. The maximum of the CO absorption is also slightly blue-shifted from that characteristic of CO isolated in solid argon, shown in trace g. However, there is a partially resolved shoulder at the position of the isolated molecule absorption. Also noteworthy is a shoulder at 1744 cm⁻¹, on the high-frequency side of the very prominent 1736-cm⁻¹ absorption of hydrogen-bonded H₂CO. Absorptions in other spectral regions were similar in position and relative intensity to those in the mercury-arc photolysis experiments, except that the 1029-cm⁻¹ absorption did not appear. On subsequent mercury-arc photolysis of the sample, the product peaks characteristic of traces b and c grew in intensity, but the absorptions of CO and NO and the 1744-cm⁻¹ shoulder were unchanged.

In experiments in which the Ar:CH₃ONO sample was codeposited with a beam of excited argon atoms, such as

(24) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, 1945, p 300.

(25) M. E. Jacox, *Chem. Phys.*, **59**, 213 (1981).

(26) H. Khoshkhoo and E. R. Nixon, *Spectrochim. Acta, Part A*, **29**, 603 (1973).

TABLE II: Peak Optical Densities of CD₃ONO Photolysis Products Trapped in Solid Argon

cm ⁻¹	$\lambda > 345^a$	$\lambda > 122^a$	$\lambda > 122^b$	$\lambda > 105^b$	assignment
1160		0.028	0.053	0.046	DNO ^d
1169	0.306	0.075	0.036	0.017	DNO ^c
1545	0.404	0.156	sh	sh	DNO ^c
1550		0.044	0.228	0.104	DNO ^d
1691	0.822	0.326	0.165	0.054	D ₂ CO ^c
1700		sh	0.094	0.060	D ₂ CO
1877	0.026	0.179	0.431	0.112	NO
2142		0.243	0.444	0.144	CO

^a Photolysis of total sample. ^b Photolysis concurrent with deposition. ^c Site I; DNO + D₂CO pair interactions. ^d Site II.

that of trace e, decomposition of the CH₃ONO can result either from collisional energy exchange with metastable argon atoms (11.5 and 11.7 eV) or from absorption of a 11.6- or 11.8-eV (107–105 nm) photon of argon resonance radiation. Under these conditions, the most prominent product absorptions are those of CO and NO, with the absorptions of HNO and of H₂CO greatly diminished in intensity. The peak optical densities of these product absorptions are summarized in the fifth column of Table I. The most prominent peak of H₂CO is shifted to 1744 cm⁻¹, the position characteristic of H₂CO isolated in solid argon. The NO-stretching absorption of HNO is shifted to 1571 cm⁻¹ (site II) and has a shoulder at 1563 cm⁻¹, the position of the isolated molecule absorption.

Important spectral regions in the corresponding experiments on Ar:CD₃ONO samples are shown in Figure 2, and the peak optical densities of product absorptions in these spectral regions are summarized in Table II. As is shown in trace a, for unphotolyzed Ar:CD₃ONO samples the 1616-cm⁻¹ absorption of the *cis* rotamer is more intense than the 1667-cm⁻¹ *trans* absorption. For all of the photolyzed samples, this intensity relationship is reversed. Portions of the spectrum observed for a sample which had been subjected to mercury-arc radiation of wavelength longer than 345 nm are shown in trace b and are summarized in the first two columns of Table II. In addition, a very strong product absorption appeared at 2083 cm⁻¹, strong absorptions at 988 and 2196 cm⁻¹, and moderately intense absorptions at 1098 and 2112 cm⁻¹. All of these peaks except that at 2112 cm⁻¹ can be assigned to D₂CO.²⁴ Comparison with trace g shows that the extremely prominent 1691-cm⁻¹ D₂CO absorption is significantly shifted from the 1700-cm⁻¹ isolated molecule absorption.²⁵ Such deviations also occur for the two CD-stretching fundamentals, assigned by Khoshkhoo and Nixon²⁶ at 2070 and 2177 cm⁻¹. Comparison with trace f also reveals a substantial deviation from the absorptions of isolated DNO, previously reported¹⁷ at 1153, 1547, and 2043 cm⁻¹.

Spectra obtained in experiments in which the deposit was prepared before the sample was exposed to 122-nm radiation and in which irradiation was concurrent with deposition are compared in traces c and d, respectively, and peak optical densities of the product absorptions in these two experiments are summarized in the third and fourth columns of Table II. In both experiments the yields of CO and NO were greatly enhanced and those of D₂CO and DNO diminished compared to typical mercury-arc photolysis experiments. New peaks attributable to DNO trapped in a different type of site, designated as site II, appeared at 1160 and 1550 cm⁻¹, and in the concurrent deposition and photolysis study these peaks were more prominent than those at 1169 and 1545 cm⁻¹. The 1700-cm⁻¹ shoulder on the 1691-cm⁻¹ D₂CO absorption also was

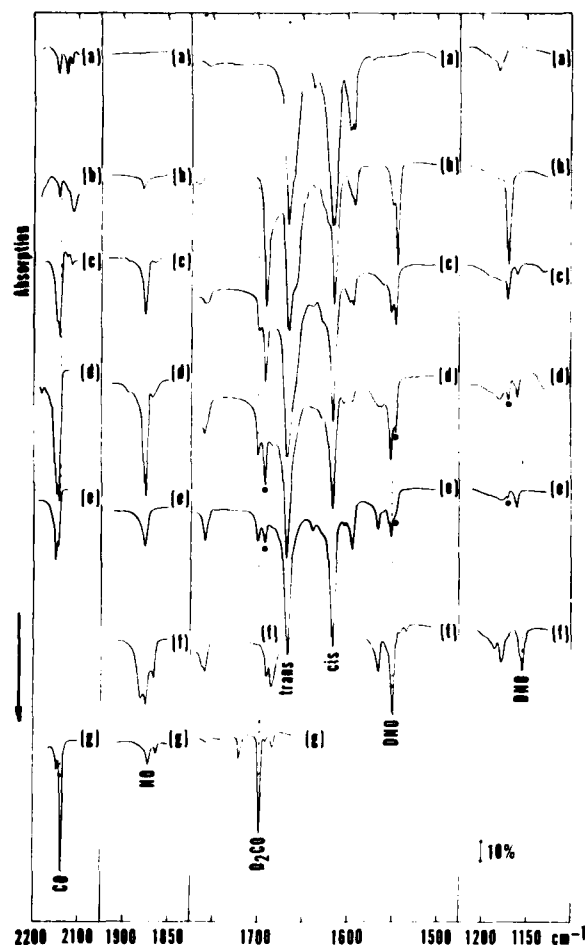


Figure 2. (a) 3.21 mmol Ar:CD₃ONO deposited at 14 K without photolysis. (b) 75-min subsequent mercury-arc photolysis ($\lambda > 345$ nm) of sample in (a). (c) 3.00 mmol Ar:CD₃ONO = 200 deposited at 14 K, then subjected to hydrogen-discharge photolysis for 218 min. (d) 3.74 mmol Ar:CD₃ONO = 200 deposited at 14 K over period of 190 min with concurrent hydrogen-discharge photolysis. (e) 2.89 mmol Ar:CD₃ONO = 200 codeposited at 14 K over period of 167 min with 2.35 mmol discharged Ar. (f) 16.4 mmol Ar:NO = 200 deposited at 14 K over period of 366 min with 19.9 mmol discharged Ar:D₂ = 200. (g) 4.39 mmol Ar:CD₃OD = 200 codeposited at 14 K over period of 291 min with 3.00 mmol discharged Ar. (●) Grows on subsequent mercury-arc photolysis.

more prominent when photolysis and deposition were concurrent.

As is shown in trace e and in the fifth column of Table II, when an Ar:CD₃ONO sample was codeposited with a beam of excited argon atoms the major products were CO and NO, and the site II DNO adsorptions were more prominent than those at 1169 and 1545 cm⁻¹. The isolated D₂CO absorption at 1700 cm⁻¹ had an intensity similar to that of the 1691-cm⁻¹ absorption. No new product absorptions appeared.

Experiments were also conducted to explore the dependence of the intensities of various absorptions of Ar:CH₃ONO and Ar:CD₃ONO deposits on the duration of photolysis by mercury-arc radiation with a 345-nm short wavelength cutoff. So that the effects due to warmup of the mercury arc could be minimized, it was turned on at least 1 h before the beginning of photolysis. The results of a typical experiment are shown in Figure 3. The absorptions of *cis*-CD₃ONO, exemplified by the peak at 1616 cm⁻¹, decreased throughout the course of the experiment.

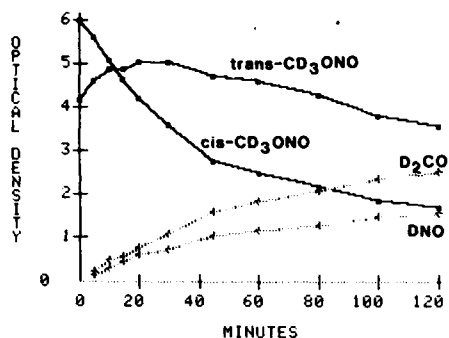


Figure 3. Time dependence of peak optical densities on mercury-arc photolysis ($\lambda > 345$ nm) of 0.5 mmol Ar:CD₃ONO = 200 deposited at 14 K: *cis*-CD₃ONO, 1616 cm⁻¹; *trans*-CD₃ONO 1667 cm⁻¹; D₂CO, 1691 cm⁻¹; DNO 1545 cm⁻¹.

The decay curve for this species is biexponential, with a slower rate of disappearance at longer photolysis times. For short photolysis times, the intensities of the *trans* absorptions, exemplified by that at 1667 cm⁻¹, grew somewhat. After about 30 min of photolysis, the *trans* absorptions also began to diminish. The strongest absorptions of D₂CO and DNO, at 1691 and 1545 cm⁻¹, respectively, were detectable after only 5 min of photolysis and grew throughout the course of the experiment.

Discussion

All of the photolysis product absorptions in these experiments can be assigned to HNO, H₂CO, NO, and CO. No absorptions attributable to CH₃O were identified, and other peaks which were prominent in the previous study,¹⁴ including those at 1109 and 3300 cm⁻¹ which had been attributed to HNO, appeared only weakly or were completely absent. Recent observations of the prolonged mercury-arc photolysis of nitromethane in an argon matrix²⁷ suggest that these peaks may be contributed by secondary photodecomposition products.

All of the studies of the gas-phase photodecomposition of methyl nitrite indicate that over a wide range of wavelengths the predominant primary products are CH₃O and NO. In solid argon, the cage recombination of these two species, each with an unpaired electron, to re-form methyl nitrite should occur with no activation energy. Tarte¹⁴ and Napier and Norrish⁴ have suggested that *trans*-CH₃ONO may absorb only weakly between 300 and 400 nm. Thus, exposure of a matrix-isolated sample containing a substantial concentration of the *cis* rotamer to radiation in this spectral region should result in a selective disappearance of the *cis* species. If the probabilities of forming the *cis* and *trans* rotamers upon cage recombination are approximately equal, the growth in the concentration of the *trans* species in the early stages of photolysis and the biexponential character of the curve for the photolysis of the *cis* species can also be explained. Deactivation of a relatively long-lived excited state of methyl nitrite may also contribute to the observed isomerization.

Recent gas-phase studies indicate that cage recombination could explain the prominence of the H₂CO and HNO absorptions in the argon matrix experiments. The reaction of CH₃O and NO to form H₂CO and HNO occurs readily at room temperature.^{12,28} Although Phillips²⁹ had

suggested that because of the requisite nuclear rearrangement this process should have a nonzero activation energy, Batt and co-workers²⁸ found its rate, as well as that for the re-formation of methyl nitrite, to be independent of temperature. The perturbations in the spectra of both H₂CO and HNO, to receive later discussion, are also consistent with a cage recombination mechanism.

It is conceivable that H₂CO and HNO are also formed by the direct decomposition of *cis*-methyl nitrite, as has been suggested by Brown and Pimentel.¹³ If the *cis* rotamer is the principal absorber between 300 and 400 nm, the formation of H₂CO and HNO as primary products might be expected to be favored in 366-nm gas-phase photolysis experiments. This prediction was not confirmed in the studies by Hecklen and co-workers.²³ Furthermore, as has been noted by Calvert and Pitts,¹ such a process should favor the formation of HON. No evidence has been obtained for the stabilization of this structure.

Several observations suggest that there may exist one or more indirectly accessible excited electronic states or a range of excited vibrational levels of ground-state methyl nitrite which may yield HNO + H₂CO as primary decomposition products. Decomposition of methyl nitrite to form H₂CO + HNO is approximately 27 kcal/mol (113 kJ/mol) more exothermic than that to form CH₃O + NO;^{30,31} the radical decomposition process is favored because of the relatively weak O-N bond. Pyrolysis studies by Phillips,²⁹ Napier and Norrish,⁴ and Batt and co-workers²⁸ have yielded some evidence for the direct formation of H₂CO. Batt has suggested a possible four-center elimination of HNO from CH₃ONO in a transition state having the *trans* configuration for the heavy atoms. Hartford³² has observed infrared fluorescence attributable to H₂CO in studies of the infrared multiphoton decomposition of methyl nitrite. The band pass of the filter used for these observations would also permit detection of fluorescence arising from the NH-stretching mode of vibrationally excited HNO.^{17,18} A contribution from the CH-stretching vibrations of CH₃O would require that they be atypically low in frequency. The time dependence of the fluorescence rise indicated that the fluorescing species is a primary product or is formed within approximately three collisions. The rate constant determined by Batt²⁸ and by Sanders¹² for the reaction of CH₃O with NO to form H₂CO and HNO is too small for a significant concentration of H₂CO to result from the secondary process.

The appearance of an enhanced concentration of isolated H₂CO and of site II HNO in the 122-nm photolysis experiments with concurrent deposition also suggests that such a manifold of energy levels may exist. Most molecules absorb 122-nm radiation very strongly, effectively screening inner layers of the deposit from radiation at this wavelength. On the other hand, the near-ultraviolet component of the hydrogen-discharge radiation can penetrate the sample, giving photolysis products similar to those in the mercury-arc studies. Since the energy of 122-nm radiation greatly exceeds the photodecomposition threshold, the radical products may be formed with a relatively high

(30) D. R. Stull and H. Prophet, Eds., "JANAF Thermodynamic Tables", 2nd ed, Natl. Stand. Ref. Data Ser., Nat. Bur. S and, (U.S.) (1971).

(31) S. W. Benson, "Thermochemical Kinetics", 2nd ed, Wiley, New York, 1976.

(32) A. Hartford, Jr., *Chem. Phys. Lett.*, **53**, 503 (1978).

(33) Certain commercial instruments and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

(27) M. E. Jacox, unpublished data.

(28) L. Batt, R. T. Milne, and R. D. McCulloch, *Int. J. Chem. Kinet.*, **9**, 567 (1977).

(29) L. Phillips, *J. Chem. Soc.*, 3082 (1961).

translational energy, enhancing the probability of their separation in the gas phase or on the surface of the sample when deposition and photolysis are concurrent. Such a process has been observed in studies of the concurrent deposition and photolysis of $\text{Ar:CF}_3\text{NNCF}_3$ samples,²² in which very high yields of CF_3 resulted. The 1700-cm^{-1} shoulder of isolated D_2CO in the experiment of Figure 2d may result from the trapping of D_2CO directly formed in the gas phase, from the photodecomposition of CD_3O formed in the gas phase and trapped in isolated sites, or from the photodecomposition of DNO trapped adjacent to D_2CO , removing the hydrogen-bonding perturbation. Of these three processes, only the last could occur in experiments in which the sample is deposited before photolysis, and this process may explain the appearance of a weak shoulder at 1700 cm^{-1} in the experiment of Figure 2c. The enhancement of the site II DNO peaks in the experiment with concurrent deposition and photolysis suggests that in site II the hydrogen-bonding perturbation of DNO (or HNO) is removed but that longer-range interactions, to which this species is extraordinarily sensitive,¹⁷ persist.

Under the conditions of the excited argon beam experiments, there is extensive decomposition to produce CO and NO, and absorptions of isolated H_2CO and of site II HNO are relatively important. Since the probability of secondary product decomposition is much smaller in argon discharge experiments than in hydrogen-discharge and mercury-arc photolysis experiments,²⁵ it is likely that the isolated H_2CO results from the decomposition of excited CH_3O or from direct fragmentation of CH_3ONO in the deposition beam. The stabilization of site II HNO would not require the formation of HNO before condensation, since H atoms may migrate through the argon lattice and react with NO.

Further consideration of the frequency shifts in an argon matrix provides information about the structure of the hydrogen-bonded complex between HNO and H_2CO . The NO-stretching and the bending fundamentals of HNO are strongly mixed. On the other hand, the potential energy distribution obtained for DNO in the previously reported¹⁷ normal coordinate calculations indicates that these two vibrations of DNO are virtually unmixed. The NO-stretching fundamental of DNO, which lies at 1547 cm^{-1} for the isolated molecule,¹⁷ appears at 1545 cm^{-1} for hydrogen-bonded DNO and at 1550 cm^{-1} for site II DNO. Thus, the NO-stretching motion is relatively insensitive to the trapping site. On the other hand, the bending vi-

bration, at 1153 cm^{-1} for the isolated molecule, appears at 1169 cm^{-1} for the hydrogen-bonded complex and at 1160 cm^{-1} for site II DNO. It may be inferred that the D atom of DNO is involved in the hydrogen bond and that the NO group is relatively unaffected. For HNO, both of the corresponding fundamentals increase in frequency because of the mixing of the NO-stretching and the bending motions. The C=O stretching frequency of H_2CO is sufficiently lowered by the interaction with HNO to suggest the participation of this group in the hydrogen bond. Comparison of the CH-stretching frequencies obtained for H_2CO with those reported by Khoshkhoo and Nixon²⁶ for isolated and aggregated H_2CO indicates that the C-H bonds of H_2CO are also perturbed in the complex. Since such a perturbation may be a consequence of the change in the bonding characteristics of the C=O group, the $\text{H}_2\text{C=O}\cdots\text{H-NO}$ structure appears reasonable for the complex observed in the present experiments.

Conclusions

The threshold for the photodecomposition of methyl nitrite isolated in solid argon lies near 370 nm , with no evidence for photoisomerization of this molecule at longer wavelengths. The behavior of the methyl nitrite absorptions on photolysis with radiation of wavelength longer than 300 nm is consistent with the suggestion of previous workers that the trans rotamer absorbs much less strongly than the cis between 300 and 400 nm . The stabilization of H_2CO and HNO is consistent with recent gas-phase studies, which have established that the primary photodecomposition products of both *cis*- and *trans*- CH_3ONO are $\text{CH}_3\text{O} + \text{NO}$ over a wide range of wavelengths and that these products recombine with zero activation energy both to re-form CH_3ONO , with randomization of the *cis* and *trans* configurations, and to form $\text{H}_2\text{CO} + \text{HNO}$. These recombination processes should also play an important role in the decomposition of methyl nitrite in other condensed-phase systems. Methyl nitrite may also possess a relatively long-lived low-lying excited electronic state or a range of vibrational energy levels of the ground state which decomposes directly into $\text{H}_2\text{CO} + \text{HNO}$. Hydrogen bonding occurs between these two molecules, which are formed in adjacent sites in the argon lattice, resulting in shifts in the positions of their infrared absorptions.

Acknowledgment. This work was supported in part by the U.S. Army Research Office under Research Proposal No. 17710-C.

Accession For	
DATE	11/11/81
BY	✓
CLASS	11
STATUS	11
Distribution/	
Availability Codes	
Dist	Special
A	21

